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CLAIMS

What is claimed is:

- 1. A near infrared sensitive composition, comprising:
 - (a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either
 - (i) effective photopolymerization or
 - (ii) effective photoimaging upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:

(D₁)(H) (H) (H)(D₂)
$$(CH2)n$$

wherein substituent A is chosen from

- having 1-3 ring heteroatoms, in which the heteroatom is a nitrogen atom, which is substituted with a hydrogen atom, C₁-C₆ alkyl, (CH₂)_mCO₂H or (CH₂)_mCO₂(C₁-C₆ alkyl) and the carbon atom of the herocyclic ring system may be substituted with an oxygen atom to form a carbonyl or enolate anion and m is an integer ranging from 0-4;
- (2) a 5-6 membered carbocyclic moiety substituted with a hydrogen atom or a C₁-C₆ alkyl group wherein a carbon atom of the alkyl group may be substituted with oxygen to form a carbonyl or enolate anion;
- (3) a quinoline or isoquinoline group wherein the nitrogen atom is directly bonded to the carbocyclic moiety of formula I;
- (4) N,N-bisaryl or bis(C_1 - C_6 alkyl) or bisaryl(C_1 - C_6 alkyl) amine wherein the aryl

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	ore	oup is a naphthyl or phenyl group which is	
	_	substituted or substituted with a fluorine	
		om, bromine atom, chlorine atom, OCH ₃ ,	
		F_3 , OH, or C_1 - C_6 alkyl;	
5		neterocyclic ring system having at least one	
		rogen atom bonded directly to the	
		rbocyclic ring of formula I and a group Z	
		nich is a carbon atom, NR ⁸ , oxygen atom or	
		Ifur atom wherein R ⁸ is a hydrogen atom,	
10		-C ₆ alkyl, CO ₂ H or CO ₂ C ₁ -C ₆ alkyl;	
	_	substitutent D ₁ is a 9-15 membered heterocyclic	
		system comprising a heteroaryl ring system having at least	
		one heteroatom group (U) which is an NR ³ group, oxygen	
	atom, sulfur atom or PR ³ group which is directly bonded		
15	to the aryl portion of the heteroaryl ring system and		
	wherein R ³ is	wherein R ³ is a C ₁ -C ₆ alkyl which may be unsubstituted	
		with CO ₂ H, SO ₃ H or salts thereof and	
	wherein the ar	yl ring may be unsubstituted or substituted	
	with OCH ₃ , C	F ₃ , bromine atom, chlorine atom, fluorine	
20	atom, C_1 - C_6 a	lkyl or OH or a fused ring polycyclic	
	hetercyclic sys	stem;	
	substitue	ent D ₂ has the identical heterocyclic system	
	as substituent	D_1 except that when U is NR ³ , the nitrogen	
	atom is quater	nized to form an amine salt which is	
25	neutralized by an enolate anion from A when A is a		
	substituted pyr	rimidine like moiety or by a discrete (non	
	intra-molecula		
	n is an ir	nteger ranging from 1-2;	
	•	dazole compound as photoinitiator;	
30	1, 1	izable material and a chain transfer agent,	
	or, instead of (c)		
	(d) a photoimageab	·	
2. A photopolymerizable element comprising:			
	(a) a support,		
35		izable composition comprising	
	**	rared dye photochemical sensitizer which is	
		bstantially free of borate anion that enables	
	the	e photopolymerizable composition to	
		• •	

undergo effective photopolymerization upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:

$$(D_1)(H)$$

$$(H)=(H)(D_2)$$

$$I$$

5 wherein A is:

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(1) a 5-6 membered heterocyclic ring system having 1-3 ring heteroatoms, in which the heteroatom is a nitrogen atom which is substituted with a hydrogen atom, C₁-C₆ alkyl, (CH₂)_mCO₂H or (CH₂)_mCO₂(C₁-C₆ alkyl) and the carbon atom of the heterocyclic ring system may be substituted with an oxygen atom to form a carbonyl or enolate anion and m is 0-4;

- (2) a 5-6 membered carbocyclic moiety substituted with hydrogen atom, C₁-C₆ alkyl group wherein the carbon atom of the alkyl group may be substituted with oxygen to form a carbonyl or enolate anion;
- (3) quinoline or isoquinoline groups wherein the nitrogen atom is directly bonded to the carbocyclic moiety of formula I;
- (4) N,N-bisaryl or bis(C₁-C₆ alkyl) or bisaryl(C₁-C₆ alkyl) amine wherein the aryl group is a napthyl or phenyl group which is unsubstituted or substituted with fluorine atom, bromine atom, chlorine atom, OCH₃, CF₃, OH, C₁-C₆ alkyl;
- a heterocyclic ring system having at least one nitrogen atom bonded directly to the carbocyclic ring of formula I and a group Z which is a carbon atom, NR⁸, oxygen atom, or sulfur atom wherein R⁸ is a hydrogen atom, C₁-C₆ alkyl, CO₂H or CO₂C₁-C₆ alkyl;

substituent D₁ is a 9-15 membered heterocyclic system comprising a

heteroaryl ring having at least one heteroatom group (U) which is an NR³ group,
oxygen atom, sulfur atom, or PR³ group which is directly bonded to the aryl
portion of the heteroaryl ring system and wherein R³ is a C₁-C₆ alkyl which may
be unsubstituted or substituted with CO₂H, SO₃H or salts thereof and wherein the

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aryl ring may be unsubstituted or substituted with OCH3, CF3, bromine atom, chlorine atom, fluorine atom, C₁-C₆ alkyl or OH or a fused ring polycyclic heterocyclic system;

substituent D_2 has the identical heterocyclic system as substituent D_1 except that when U is NR3, the nitrogen atom is quaternized to form an amine salt which is neutralized by an enolate anion from A when A is a substituted pyrimidine like moiety or by a discrete (non intra-molecular) anion;

n is an integer ranging from 1-2;

- a hexaarylbiimidazole compound as photoinitiator; (c)
- a photopolymerizable material and a chain transfer agent; (d) and
- (e) a binder polymer.
- 3. A near infrared sensitive composition, comprising:
 - a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either
 - (i) effective photopolymerization or
 - (ii) effective photoimaging upon exposure to near infrared radiation, the near infrared dye is a compound of formula I:

$$(D_1)(H)$$
 $(H)=(H)(D_2)$

$$R^2$$
 R^1
 R^2
 R^1
 R^2
 R^1
 R^2
 R^2

D1 is:
$$(Ar)$$
 ; or (Ar) (Y) (Ar) (Y)

D2 is
$$(Y)$$
 $R^{4}-R^{7}$; or (Y) het $R^{4}-R^{7}$

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 $\rm R^1$ or $\rm R^2$ are independently selected from H, C₁-C₆ alkyl; or aryl wherein aryl is phenyl or napthyl which may be unsubstituted or substituted with halogen, -O(C₁-C₆ alkyl), -Oaryl, aryl or CF₃; (C₁-C₆ alkyl) (C₁-C₁₀ aryl) or hydrogen;

Ar is an aromatic ring chosen from phenyl or napthyl;

het

is a heteroaryl ring chosen from benzopyrazine, benzo-1,4-oxazine or benzo-1,4-thiazine.

U is selected from NR³, S, PR³ or O; Y is selected from C(R¹)(R²);

$$R^1$$
 or U, wherein R^1 and R^2 are as defined above;

 R^3 is selected from C_1 - C_6 alkyl unsubstituted or substituted with CO_2H , SO_3H or salts thereof;

R⁴-R⁷ are independently chosen from H, OCH₃, CF₃, halogen; Z is chosen from NR⁸, C, O or S;

 R^8 is chosen from H, C_1 - C_6 alkyl, $(CH_2)_mCO_2H$ or $(CH_2)_mCO_2(C_1$ - C_6 alkyl); and

m is 0-6;

n is 1-2;

provided that when A contains an enolate anion, a counterion L^{Θ} is not present;

- (b) a hexaarylbiimidazole compound as photoinitiator;
- (c) a photopolymerizable material and a chain transfer agent; or, instead of (c),
- (d) a photoimageable dye.
- 4. A photopolymerizable element comprising:
 - (a) a support;
 - (b) a photopolymerizable composition comprising
 - (i) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the photopolymerizerable composition to undergo effective photopolymerization upon exposure to neared infrared radiation, the near infrared dye is a compound of formula I:

$$(D_1)(H)$$
 (H)
 (H)
 (H)
 (H)
 (H)
 (H)
 (H)
 (H)

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C1-C6
$$C1$$
-C6 $C1$ -C6 $C1$ -C6 $C1$ -C6 $C1$ -C6 $C1$ -C7 $C1$ -C6 $C1$ -C7 $C1$ -C8 $C1$ -C8 $C1$ -C8 $C1$ -C9 $C1$ -C9 $C1$ -C9 $C1$ -C6 $C1$ -C9 $C1$ -C1 $C1$ -C1

 D_1 represents a heterocyclic ring structure selected from the group consisting of:

$$R^5$$
 R^4
 R_1
 R_2
 R_3

 R^5 R^4 R^5 R^6 R^7 R^8 R^7 R^8 R^8 R^8

 D_2 represents a heterocyclic ring structure selected from the group consisting of

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R¹ or R² are independently selected from:

 C_1 - C_6 alkyl, aryl wherein aryl is phenyl or napthyl which may be unsubstituted or substituted with halogen, -O(C_1 - C_6 alkyl), Oaryl, aryl or CF₃, (C_1 - C_6 alkyl) aryl or hydrogen;

R3 is C_1 - C_6 alkyl, C_1 - C_6 alkylsulfonate, C_1 - C_6 alkyloxycarbonyl, C_1 - C_6 alkyl, or C_1 - C_6 alkylcarboxy;

Z is selected from NR⁸, C, O or S wherein R⁸ is H, C_1 - C_6 alkyl, CO_2H or $CO_2(C_1$ - C_6 alkyl);

 R^4 - R^7 are independently selected from H, OCH₃, CF₃; or any two of R^4 - R^7 which when ortho substituents may join to form a phenyl ring; n is an integer ranging from 1-2

with the proviso that D_2 is selected to be the quaternized heterocyclic ring structure that corresponds to D_1 such that D_1 and D_2 together form a pair of heterocyclic ring structures;

- (c) a hexaarylbiimidazole compound as photoinitiator;
- (d) a photopolymerizable material and a chain transfer agent; and
- (e) a binder polymer.
- 5. A near infrared sensitive composition, comprising:
- (a) a near infrared dye photochemical sensitizer which is substantially free of borate anion that enables the composition to undergo either
 - (i) effective photopolymerization or
 - (ii) effective photoimaging upon exposure

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to near infrared radiation wherein the near infrared dye is selected from the group consisting of DF-1413, DF-1419, DF-1422, DF-1429, DF-1668, DF-12124, DF-15118, DF-15131, DF-15132, NK-3877, GW-826, GW-436, GW-776, GW-976, GW-186, and NK-2268;

- (b) a hexaarylbiimidazole compound selected from the group consisting of o-Cl-HABI, CDM-HABI, 2,3,5-TCl-HABI, and TCTM-HABI; and
- (c) a photopolymerizable material selected from the group consisting of tripropylene glycol diacrylate, trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, ethoxylated Bisphenol A dimethacrylate, and triethylene glycol dimethacrylate, and a chain transfer agent selected from the group consisting of N-phenylglycine, julolidine, 2-mercaptobenzoxazole, 2,6-diisopropyl-N,N-dimethylaniline, a borate salt and an organic thiol.
- 6. The composition according to Claim 3 wherein A is selected from the group consisting of

 D_1 represents a heterocyclic ring structure selected from the group consisting of

$$R^{5}$$
 R^{6}
 R^{7}
 R^{3}
 R^{6}
 R^{7}
 R^{3}
 R^{4}
 R^{7}
 R^{3}
 R^{5}
 R^{6}
 R^{7}
 R^{3}
 R^{6}
 R^{7}
 R^{8}
 R^{7}
 R^{8}
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 R^{8}
 R^{7}
 R^{8}
 R^{8}
 R^{8}

 D_2 represents a heterocyclic ring structure selected from the group consisting of

$$R_3$$
 R_7 R_6 R_8 R_7 R_8 R_8 R_7 R_8 R_8

 R_1 or R_2 are independently selected from: C_1 - C_6 alkyl;

aryl wherein aryl is phenyl or napthyl which may be unsubstituted or substituted with halogen, $-O(C_1-C_6 \text{ alkyl})$, Oaryl, aryl or phenyl, CF_3 ($C_1-C_6 \text{ alkyl}$)($C_1-C_{10} \text{ aryl}$) or hydrogen;

R3 is C_1 - C_6 alkyl, C_1 - C_6 alkylsulfonate, C_1 - C_6 alkyloxycarbonyl, C_1 - C_6 alkyl, or carboxy C_1 - C_6 alkyl;

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Z is selected from NR⁸, C, O or S wherein R⁸ is H, C_1 - C_6 alkyl, CO_2H or $CO_2(C_1$ - C_6 alkyl);

 R^4 - R^7 are independently selected from H, OCH₃, CF₃; or any two of R^4 - R^7 which when ortho substituents may join to form a phenyl ring;

- with the proviso that D_2 is selected to be the quaternized heterocyclic ring structure that corresponds to D_1 such that D_1 and D_2 together form a pair of heterocyclic ring structures.
- The composition according to Claim 3, wherein the near infrared dye is selected from the group consisting of DF-1413, DF-1419, DF-1422, DF-1429, DF-1668, DF-12124, DF-15118, DF-15131, DF-15132, NK-3877, GW-826, GW-436, GW-776, GW-976, GW-186, and NK-2268; the hexaarylbiimidazole compound is selected from the group consisting of o-Cl-HABI, CDM-HABI, 2,3,5-TCl-HABI, and TCTM-HABI; wherein the photopolymerizable material is selected from the group consisting of tripropylene glycol diacrylate,
- trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, ethoxylated Bisphenol A dimethacrylate, and triethylene glycol dimethacrylate, and the chain transfer agent is selected from the group consisting of N-phenylglycine, julolidine,
 2-mercaptobenzoxazole, 2,6-diisopropyl-N,N-dimethylaniline, and an organic
 thiol; or the photoimageable dye is selected from the group consisting of LCV,
 LECV, LPCV, LBCV, LV-1, LV-2 and LV-3.
 - 8. The composition according to Claims 1, 2, 3 or 4 wherein the near infrared dye is present in at least 0.5% by weight of the total composition; the hexaarylbiimidazole compound is present in at least 0.5% by weight of the total composition; and the photopolymerizable material is present in at least 20% by weight of the total composition and the chain transfer agent is present in at least 0.1% by weight of the total composition; or the photoimageable dye is present in at least 0.5% by weight of the total composition.
- 9. The composition according to Claims 1, 2, 3, 4 or 5 which further comprises a binder polymer.
 - 10. The composition according to Claims 1, 2, 3 or 4 wherein the composition, containing at least 0.5 weight percent of the near infrared dye, undergoes either (1) effective photopolymerization or (2) effective photoimaging to a photopolymerized or photoimaged photopolymer upon exposure to near infrared actinic radiation at a fluence of at least 100 mW/cm² (fluence units) for a period of at least 2 seconds (time units).